(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 505 061 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 92301914.5

(22) Date of filing: 05.03.92

(51) Int. Cl.5: C03C 3/091, C03C 3/095, H01L 31/048

(30) Priority: 22.03.91 GB 9106086

(43) Date of publication of application: 23.09.92 Bulletin 92/39

(84) Designated Contracting States: BE DE ES FR GB IT NL SE

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(54) **Borosilicate glass composition.**

(57) A borosilicate glass composition characterised in that the glass composition consists essentially of the following components:-

SiO_2	57 - 77 mol%,
Al_2O_3	0 - 8.5 mol%,
B_2O_3	4.6 - 23.0 mol%,

the total amount of SiO_2 + Al_2O_3 + B_2O_3 being from 81 to 91 mol%,

Li_2O	0 - 1.5 mol%,
Na_2O	2 - 7.5 mol%,
K_2O	2 - 7.5 mol%,

the total amount of Li_2O + Na_2O + K_2O being from 7.6 to 10.6 mol%,

CeO_2	0.7 - 2.0 mol%,
Sb_2O_3	0 - 0.3 mol%,
As_2O_3	0 - 0.3 mol%,
TiO_2	0 - 2.0 mol%,
F_2	0 - 2.0 mol%,

and one or more of MgO, CaO, SrO, BaO, ZnO and PbO, in a total amount of from 0 to 7 mol%;
and in that the glass composition exhibits a coefficient of linear expansion within the range 64.0 - 70.0 x 10^{-7}/deg.C.

These glass compositions are intended for use in making protective covers for gallium arsenide solar cells.

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The present invention relates to borosilicate glass compositions. More particularly, the invention relates to borosilicate glass compositions which incorporate cerium oxide and which are suitable for use as protective covers for solar cells, especially solar cells constructed from gallium arsenide for use in satellites.

US Patent 4 746 634 describes a range of borosilicate glass compositions for use in the protection of silicon solar cells. They have coefficients of linear expansion in the range 73.5 - 76.7 x 10^{-7}/deg.C. In our earlier European Patent 0261885 we describe an improved range of borosilicate glass compositions having coefficients of linear expansion which match the coefficient of linear expansion of silicon.

The need to match the coefficient of linear expansion of the glass composition to that of a substrate, e.g. a silicon substrate, arises from the need to bond a protective cover made from said glass composition directly to the solar cell.

Furthermore, in order to be suitable for use in making such protective covers for solar cells, the glass compositions must be capable of being produced in the form of thin sheets of glass having a thickness of from 50 to 500 microns.

A protective cover made from such glass compositions must also exhibit the following properties:

(i) good spectral transmission with at least 80% of incident light being transmitted at 400 nm and 85% of incident light being transmitted at 450 nm (for a sample having a thickness in the range of 50 to 500 microns);

(ii) low ultra-violet light transmission i.e. high UV absorption at wavelengths below 320 nm, with less than 5% incident radiation being transmitted, more preferably less than 2% incident radiation being transmitted (for a sample having a thickness in the range of 50 to 500 microns); and

(iii) absence of significant discolouration (also known as radiation stability) when exposed to solar radiation of space which comprises, inter alia, ultra-violet light, low energy electrons, protons, X-rays and gamma rays.

Solar energy cells constructed from gallium arsenide are being developed for use in space satellites. Such cells can be glazed with protective covers if made from known glass compositions provided that an adhesive layer is used to bond the protective cover to the solar cell. However, if it is desired to bond the protective cover directly to the solar cell, then the glass must have a coefficient of linear expansion which is the same as, or very close to, that of the material from which the solar cell is made.

Experiments have shown that for direct bonding to gallium arsenide, a coefficient of linear expansion of between 64.0 and 70.0 x 10^{-7}/deg.C is required. A match of coefficient of linear expansion is particularly important for gallium arsenide because of its fragility and brittleness.

It is well known that high stability to space radiation can be achieved by the inclusion of cerium oxide in the glass composition used to form the protective cover. From about 2 to 5% by weight cerium oxide, preferably more than 3% by weight cerium oxide, is known to have the desired effect for protective covers for silicon cells. In order to be able to manufacture sheets of glass which are sufficiently thin to be suitable for use as protective covers for solar cells, it is necessary to keep the liquidus temperature of the glass composition (in relation to the viscosity of the melt) at a low value. The presence of cerium oxide at the preferred concentration range of 2 to 5% by weight generally causes the liquidus temperature of the glass to be increased above the liquidus temperature of the cerium-free base glass composition. This is particularly true when the glass composition contains a high proportion of the more acidic network-forming oxides such as SiO_2 or B_2O_3 or Al_2O_3. Unfortunately, to prevent the coefficient of linear expansion from rising above the desired upper limit of 70.0 x 10^{-7}/deg.C it is necessary to work with glass compositions which contain relatively high concentrations of these acidic oxides and this can lead to glass compositions which have relatively high, undesirable, liquidus temperatures.

We have found a narrow range of borosilicate glass compositions which have the desired radiation stability and light transmission, a coefficient of linear expansion within the desired range and which also have liquidus temperatures which are sufficiently low in relation to the viscosity of the melt to make the glass compositions suitable for the manufacture of sheets of glass which are sufficiently thin for use as protective covers for solar cells made of gallium arsenide.

According to a first aspect of the present invention, there is provided a borosilicate glass composition characterised in that the glass composition consists essentially of the following components:-

SiO_2	57 - 77 mol%,
Al_2O_3	0 - 8.5 mol%,
B_2O_3	4.6 - 23.0 mol%,

the total amount of SiO_2 + Al_2O_3 + B_2O_3 being from 81 to 91 mol%,

Li_2O	0 - 1.5 mol%,
Na_2O	2 - 7.5 mol%,
K_2O	2 - 7.5 mol%,

the total amount of Li_2O + Na_2O + K_2O being from 7.6 to 10.6 mol%,

CeO_2	0.7 - 2.0 mol%,
Sb_2O_3	0 - 0.3 mol%,
As_2O_3	0 - 0.3 mol%,
TiO_2	0 - 2.0 mol%,
F_2	0 - 2.0 mol%,

and one or more of MgO, CaO, SrO, BaO, ZnO and PbO, in a total amount of from 0 to 7 mol%; and in that the glass composition exhibits a coefficient of linear expansion within the range 64.0 - 70.0 x 10^{-7}/deg.C.

In a particularly preferred group of glass compositions in accordance with the invention the amounts of SiO_2, Al_2O_3 and B_2O_3 fall in the following ranges:-

SiO_2	65 - 70 mol%,
Al_2O_3	0 - 2 mol%,
B_2O_3	8 - 22 mol%.

Cerium may be introduced as either the oxidised ceric form (CeO_2 - often referred to as ceric oxide) or as the reduced cerous form (Ce_2O_3). In the glass both oxide forms are often present, regardless of how the cerium is added, but the reduced cerous form Ce_2O_3 generally predominates. However, because ceric oxide (CeO_2) is the most common source of cerium, it is common practice to express cerium contents as if all the cerium is present as CeO_2.

Advantageously, the quantities of MgO, CaO, SrO, BaO, ZnO, PbO in the glass compositions of the invention fall within the following ranges:-

MgO	0-5 mol%,
CaO	0-3.5 mol%,
SrO	0-2 mol%,
BaO	0-2 mol%,
ZnO	0-2.5 mol%,
PbO	0-7 mol%.

The preferred range of the sum total of MgO + CaO + SrO + BaO + ZnO + PbO is from 0 to 3.5 mol%.

According to a further aspect of the invention there is provided a protective cover for a gallium arsenide solar cell, the cover being made from a borosilicate glass composition according to the first aspect of the invention.

Typically, the thickness of such protective covers will be within the range 50 to 500 microns. The thickness of the glass sheet will partly be governed by the composition of the glass. For example, some compositions have a colouration which is too dark to be suitable for making glass sheet having a thickness at the upper region of the quoted thickness range.

We have found that for producing glass sheet which is thinner than about 100 microns the total amount of CeO_2 + TiO_2 (ceria + titania) needs to be high, typically greater than 1.5 mol%, to give the required UV absorption. However, many such compositions with more than 1.5% CeO_2 + TiO_2 will be coloured too darkly to be suitable for the thicker glass sheet (ie. having a thickness above about 150 microns). These high UV absorbing glasses may be bleached to some extent by increasing the concentration of antimony oxide to value of above 0.3%, but maximum levels of CeO_2 + TiO_2 are not necessary for the thicker covers (i.e. above about 150 microns in thickness) and it would therefore also be possible to use CeO_2 + TiO_2 levels below 1.5% in these cases.

Bonding techniques that can be used for the glass compositions of the present invention are electrostatic bonding, teflon bonding and rigid adhesive bonding.

The present invention is illustrated by the following Examples. Table 1 shows the compositions in terms of mol percentages, whereas Table 2 shows the same compositions as Table 1, but the components in Table 2 are shown in weight percentages, based on the total weight of the glass composition.

The glass compositions in each of the examples exhibited a coefficient of linear expansion within the range

64 to 70 x 10^{-7}/deg.C.

In the following Tables:-

CLE represents the coefficient of linear expansion of the glass composition measured at 20 - 550°C (x10^{-7}/deg.C),

Tg represents the glass transition temperature (in°C), and

Tw represents the working point (in°C).

TABLE 1

	1	2	3	4	5	6	7	8
SiO2	75.0	69.2	73.2	69.3	64.3	76.8	75.9	67.6
Li2O	1.1							
Na2O	5.8	7.3	6.8	6.4	6.8	6.4	7.2	2.5
K2O	2.5	2.75	3.0	2.8	3.0	2.5	2.5	5.8
MgO	1.0							
CaO	1.0							
SrO								
BaO	0.35	0.4				0.9	0.9	
ZnO	2.25					2.4	2.4	
PbO			3.8	1.2	3.8			
Al2O3	1.3	0.6	0.14	0.14	0.14	1.3	1.3	
B2O3	7.5	18.5	11.1	18.1	20.3	8.0	8.0	22.6
Sb2O3	0.15					0.1	0.1	0.25
CeO2	1.9	0.75	1.2	1.2	0.8	1.7	1.7	0.75
TiO2	0.25	0.4	0.9	0.8	0.9			
F2								0.5
Si+Al+B	83.8	88.3	84.4	87.5	84.7	86.1	85.2	90.2
CLE	67.7	65.0	65.4	64.0	69.8	65.0	68.8	67.1
Liquidus°C	1105	940	1055	1010	970	1080	1080	960
Tg	550	530	551	532	518	580	581	496
Tw	1105	950	970	948	880	1100	1083	975

TABLE 1

	9	10	11	12	13	14	15	16
SiO_2	68.2	75.8	67.5	75.3	68.3	67.1	67.7	66.2
Li_2O				1.1	1.1			
Na_2O	2.7	6.4	2.1	6.1	2.6	2.2	2.0	2.1
K_2O	6.4	2.4	5.9	2.1	6.4	6.6	6.5	6.5
MgO								
CaO								
SrO								
BaO		0.9		0.9				
ZnO		2.4		2.4				
PbO								
Al_2O_3		1.3		1.3				
B_2O_3	21.7	8.0	22.7	8.0	20.7	22.1	21.8	22.4
Sb_2O_3	0.2	0.1	0.2	0.1	0.2	0.2	0.2	0.2
CeO_2	0.75	1.7	0.8	1.7	0.8	1.0	1.0	1.0
TiO_2								0.8
F_2		1.4	0.9	1.3		0.9	0.9	0.7
Si+Al+B	89.9	85.1	90.2	84.6	89.0	89.2	89.5	88.6
CLE	68.1	67.1	67.2	67.5	66.7	68.9	67.5	68.0
Liquidus°C	970	1075	960	1075	950	995	995	990
Tg	527	544	493	530	530	495	495	500
Tw	970	1078	975	1050	955	960	965	955

TABLE 1

	17	18	19	20	21	22	23	24
SiO_2	65.3	64.8	61.9	62.8	65.4	64.6	63.8	73.0
Li_2O								1.1
Na_2O	2.1	2.1	2.1	2.1	2.2	2.2	2.2	6.1
K_2O	6.6	6.5	6.4	6.5	6.6	6.6	6.6	2.4
MgO		1.6	4.9					
CaO				3.5				2.3
SrO					0.6	1.3	2.0	
BaO								0.85
ZnO								2.4
PbO								
Al_2O_3								1.3
B_2O_3	22.4	22.3	22.0	22.3	22.5	22.6	22.7	8.0
Sb_2O_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1
CeO_2	1.0	0.95	0.95	0.95	1.0	1.0	1.0	1.7
TiO_2	1.7	0.8	0.8	0.8	0.8	0.8	0.8	
F_2	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Si + Al + B	87.7	87.1	83.9	85.1	87.9	87.2	86.5	82.3
CLE	69.0	64.2	65.7	66.6	66.7	67.8	68.8	68.1
Liquidus °C	990	995	1000	970	970	960	970	1090
Tg	504	505	528	551	523	527	545	532
Tw	945	948	933	925	950	940	940	1030

TABLE 1

	25	26	27	28	29	30	31	32
SiO_2	75.7	62.1	57.9	72.1	73.8	75.7	70.6	73.6
Li_2O	1.1					1.1		
Na_2O	6.3	2.2	2.2	4.8	6.2	7.0	3.3	6.8
K_2O	2.5	6.6	5.4	3.2	3.0	2.5	7.2	3.0
MgO		1.7				1.0		
CaO			1.2			1.0		
SrO	1.3							
BaO	0.9					0.3		
ZnO						2.2		
PbO				6.7	3.7		1.2	3.8
Al_2O_3	1.3	2.0	8.2	0.15	0.14	1.3	0.13	0.14
B_2O_3	8.3	22.5	23.4	10.8	10.0	4.6	15.54	10.1
Sb_2O_3	0.1	0.2	0.24			0.15		
CeO_2	1.8	1.0	1.0	1.3	1.2	1.9	1.2	1.6
TiO_2		0.8	0.4	0.9	0.9	0.2	0.85	0.9
F_2	0.7	1.1			1.1	1.0		
Si+Al+B	85.3	86.6	89.5	83.0	83.9	81.6	86.2	83.8
CLE	67.4	67.4		67.7	68.7	67.7	67.3	68.7
Liquidus ^oC	1070	980	1160	1020	1030	1140	1010	1040
Tg	539	506	504	530	532	545	545	542
Tw	1010	945	1090	977	970	1075	990	975

TABLE 2

	1	2	3	4	5	6	7	8
SiO_2	69.3	64.5	62.8	62.8	54.8	70.1	69.3	62.0
Li_2O	0.5							
Na_2O	5.5	7.0	6.0	6.0	6.0	6.0	6.8	2.4
K_2O	3.6	4.0	4.0	4.0	4.0	3.5	3.5	8.4
MgO	0.6							
CaO	0.9							
SrO								
BaO	0.8	1.0				2.0	2.0	
ZnO	2.8					3.0	3.0	
PbO			12.0	4.0	12.0			
Al_2O_3	2.0	1.0	0.2	0.2	0.2	2.0	2.0	
B_2O_3	8.0	20.0	11.0	19.0	20.0	8.5	8.5	24.0
Sb_2O_3	0.7					0.4	0.4	1.0
CeO_2	5.0	2.0	3.0	3.0	2.0	4.5	4.5	2.0
TiO_2	0.3	0.5	1.0	1.0	1.0			
F_2								0.3

TABLE 2

	9	10	11	12	13	14	15	16
SiO_2	62.3	69.5	62.2	69.2	62.8	61.2	61.8	60.1
Li_2O				0.5	0.5			
Na_2O	2.5	6.0	2.0	5.8	2.5	2.1	1.9	2.0
K_2O	9.2	3.5	8.5	3.5	9.2	9.4	9.3	9.3
MgO								
CaO								
SrO								
BaO		2.0		2.0				
ZnO		3.0		3.0				
PbO								
Al_2O_3		2.0		2.0				
B_2O_3	23.0	8.5	24.2	8.5	22.0	23.3	23.0	23.5
Sb_2O_3	1.0	0.4	1.0	0.4	1.0	1.0	1.0	1.0
CeO_2	2.0	4.5	2.0	4.5	2.0	2.5	2.5	2.5
TiO_2								1.0
F_2		0.6	0.5	0.6		0.5	0.5	0.4

TABLE 2

	17	18	19	20	21	22	23	24
SiO_2	59.1	59.1	57.1	57.1	59.1	58.1	57.1	67.2
Li_2O								0.5
Na_2O	2.0	2.0	2.0	2.0	2.0	2.0	2.0	5.8
K_2O	9.3	9.3	9.3	9.3	9.3	9.3	9.3	3.5
MgO		1.0	3.0					
CaO				3.0				2.0
SrO					1.0	2.0	3.0	
BaO								2.0
ZnO								3.0
PbO								
Al_2O_3								2.0
B_2O_3	23.5	23.5	23.5	23.5	23.5	23.5	23.5	8.5
Sb_2O_3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.4
CeO_2	2.5	2.5	2.5	2.5	2.5	2.5	2.5	4.5
TiO_2	2.0	1.0	1.0	1.0	1.0	1.0	1.0	
F_2	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4

TABLE 2

	25	26	27	28	29	30	31	32
SiO_2	67.2	56.1	50.2	57.8	63.7	70.5	62.8	62.8
Li_2O	0.5					0.5		
Na_2O	5.8	2.0	2.0	4.0	5.5	6.7	3.0	6.0
K_2O	3.5	9.3	7.3	4.0	4.0	3.6	10.0	4.0
MgO		1.0				0.6		
CaO			1.0			0.9		
SrO	2.0							
BaO	2.0					0.8		
ZnO	3.0					2.8		
PbO				20.0	12.0		4.0	12.0
Al_2O_3	2.0	3.0	12.0	0.2	0.2	2.0	0.2	0.2
B_2O_3	8.5	23.5	23.5	10.0	10.0	5.0	16.0	10.0
Sb_2O_3	0.4	1.0	1.0			0.7		
CeO_2	4.5	2.5	2.5	3.0	3.0	5.0	3.0	4.0
TiO_2		1.0	0.5	1.0	1.0	0.3	1.0	1.0
F_2	0.4	0.6			0.6	0.6		

Claims

1. A borosilicate glass composition characterised in that the glass composition consists essentially of the following components:-

SiO_2	57 - 77 mol%,
Al_2O_3	0 - 8.5 mol%,
B_2O_3	4.6 - 23.0 mol%,

the total amount of SiO_2 + Al_2O_3 + B_2O_3 being from 81 to 91 mol%,

Li_2O	0 - 1.5 mol%,
Na_2O	2 - 7.5 mol%,
K_2O	2 - 7.5 mol%,

the total amount of $Li_2O + Na_2O + K_2O$ being from 7.6 to 10.6 mol%,

CeO_2	0.7 - 2.0 mol%,
Sb_2O_3	0 - 0.3 mol%,
As_2O_3	0 - 0.3 mol%,
TiO_2	0 - 2.0 mol%,
F_2	0 - 2.0 mol%,

and one or more of MgO, CaO, SrO, BaO, ZnO and PbO, in a total amount of from 0 to 7 mol%;

and in that the glass composition exhibits a coefficient of linear expansion within the range 64.0 - 70.0 x 10^{-7}/deg.C.

2. A glass composition according to claim 1, wherein the amounts of SiO_2, Al_2O_3 and B_2O_3 fall in the following ranges:-

SiO_2	65 - 70 mol%,
Al_2O_3	0 - 2 mol%,
B_2O_3	8 - 22 mol%.

3. A glass composition according to claim 1 or 2, wherein the amount of MgO is from 0 to 5 mol%.

4. A glass composition according to claim 1, 2 or 3, wherein the amount of CaO is from 0 to 3.5 mol%.

5. A glass composition according to any one of the preceding claims, wherein the amount of SrO is from 0 to 2 mol%.

6. A glass composition according to any one of the preceding claims, wherein the amount of BaO is from 0 to 2 mol%.

7. A glass composition according to any one of the preceding claims, wherein the amount of ZnO is from 0 to 2.5 mol%.

8. A glass composition according to any one of the preceding claims, wherein the amount of PbO is from 0 to 7 mol%.

9. A glass composition according to any one of the preceding claims, wherein the sum total of MgO + CaO + SrO + BaO + ZnO + PbO is from 0 to 3.5 mol%.

10. A protective cover for a gallium arsenide solar cell, the said cover being made from a borosilicate glass as claimed in any one of the preceding claims.